International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No.2, pp : 88-90 01 April 2013

Thermally Stimulated Relaxation and Electrical Conduction Phenomena In Polyacrylamide

K. Rajendra Prasad
Department of Physics, Kakatiya Institute of Technology & Science, Warangal (A.P.), India
krpkits@gmail.com

ABSTRACT

Thermally stimulated relaxation (TSR), employing thermally stimulated luminescence (TSL) and thermally stimulated conductivity (TSC) as experimental techniques, in Polyacrylamide (PAA) have been studied; in the temperature range 300 - 480 K. Measurements of electrical conductivity (σ) at various temperatures, in the same temperature range have been made, in both as-grown and UV-irradiated PAA films; to elucidate the mechanism of charge transport in relation to the macromolecular relaxations in PAA. Two TSL and TSC glow curves with maxima at 375 and 475 K have been observed. The logσ vs 1/T plots showed two transition temperatures with changes in slopes; indicating the on-set of molecular motion in PAA. The TSL/TSC curves at 475 K are attributed to the α-relaxation near the glass transition temperature of the polymer. The β-relaxation is considered to be associated with the glow curve at 375 K. Analysis of TSL / TSC curves and electrical conductivity plots have been made and the results are correlated. The two endothermic peaks recorded by Differential scanning calorimetry (DSC) are correlated with the TSL/TSC α and β - relaxations in Polyacrylamide.

Keywords. Thermally stimulated relaxation; luminescence; Electrical conductivity; Differential Scanning Calorimetry**.**

I. INTRODUCTION

Thermally stimulated relaxation (TSR) phenomena in synthetic high polymers have been investigated by several workers; mainly to identify the radiation products, understand the nature of charge carriers, traps, luminescence centers and study the kinetics of growth and decay of charge carriers etc. (1,2). Further, these techniques also have been applied to investigate crystallinity in polymers (3,4) and to elucidate the influence of molecular motion on the process of detrapping of charge carriers and study the structural transitions in polymers (5,6). This article reports the experimental results of investigation on TSR in PAA; inconjunction with the measurements of electrical conductivity; to understand the mechanism of charge transport in relation to the macromolecular relaxation and transitions in PAA. Analysis of TSL and TSC curves and electrical conductivity plots have been made, to evaluate activation energies. The relaxation processes are correlated with the results derived from differential scanning calorimetry.

II. EXPERIMENTAL

Commercially available Polyacrylamide (PAA) in the form of powder (molecular weight $\approx 5x10^6$) supplied by BDH, England, has been employed in the present studies. Thin transparent polymer films of PAA could be obtained by evaporating a solution of PAA in distilled water, on glass slides. Xenon UV-lamp (300W) was used to irradiate the PAA films.

TSL spectra of PAA were recorded by placing the UV-irradiated sample in a light tight box; in front of a photomultiplier RCA - 931A. The output current of photomultiplier was measured by an electrometer amplifier (Keithley model 610C). TSC spectra of UV-irradiated PAA films were recorded; by keeping the film in between two metal electrodes to which a suitable voltage was applied. The resulting current was measured by connecting the electrometer amplifier in series with metal electrodes. The polymer film was held firmly in between the electrodes using a spring load arrangement. The sample assembly was kept in an oven to vary the temperature. TSL and TSC spectra were recorded with a heating rate of 5^0 min^{-1}.

Electrical conductivity measurements of PAA (as-grown and UV-irradiated) were carried out, employing four point probe method (7). The four contacts used to measure conductivity, were of point contact type and were arranged as a linear array. The surface on which the probes rest was mechanically lapped to ensure good electrical contact. The probes had an equal spacing of ≈ 0.2cm and the tips of the probes were coated with zinc; which provide good electrical contact with the film. Different voltages (V) were applied to outer two probes and resulting current was measured, by connecting electrometer amplifier in series with the inner two probes. The sample holder with four probes was kept in an oven to vary the temperature of the specimen. The temperature could be monitored to an accuracy of ≈ 1^0C, employing the digital temperature controller. The samples were stabilized to any desired set temperature, prior to the

actual conductivity measurements. Electrical conductivity (σ) was evaluated using the expression σ = I/2ΠSV; where I is the current in amperes, V is the applied voltage in volts and S is the probe spacing in cm.

Differential scanning calorimetry (DSC) thermogram of PAA has been recorded on Mettler Toledo (Switzerland) equipment.

III. RESULTS AND DISCUSSION

The TSL spectra (figure 1),for UV-irradiated PAA in the temperature range 300-490 K, shows two glow peaks maxima at 375 and 475 K. Curves a, b and c are the spectra recorded for different irradiation doses; the dose of irradiation being controlled by the time of irradiation. The intensities of these glow curves are found to increase with the dose of irradiation. The TSC spectra of PAA (figure 2) show two maxima at 375 and 475K. The intensities of these TSC curves are found to increase with the dose of irradiation.

The electrical conductivity (σ), in as-grown and UV-irradiated PAA films, has been measured at various temperatures, using four-probe method. Arrhenius plots (log σ vs 1/T) are as shown in figure 3, which show enhancement of conductivity at all the temperatures of observation, on irradiation of PAA. These plots clearly indicated three distinct regions marked I, II and III; with changes in slopes at specific temperatures; indicating the on-set of macromolecular relaxations in the polymer, on thermal stimulation.

During irradiation of the polymer, charge carriers such as electrons, free radicals, ions, radical-ions or other oligomeric charged species are generated and are trapped in the solid polymer matrix. On subsequent thermal stimulation and on-set of molecular motion due to rotation of pendent groups or side chains (known as secondary or β-relaxation) ; facilitate the process of detrapping of charged species and are considered to be associated with the appearance of the TSL glow peak at 375 K. As the temperature is further increased; the on-set of large scale macromolecular motion involving the motion of the polymer back-bone chain: enable the process of detrapping of charged species. This primary relaxation (α-relaxation) which is near the glass transition temperature of PAA is considered to be associated with the TSL glow curve at 475 K.

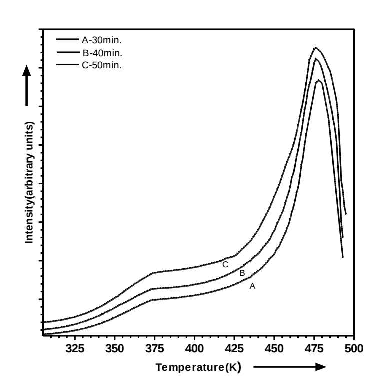


Fig 1.Thermally stimulated luminescence (TSL) spectra of Polyacrylamide

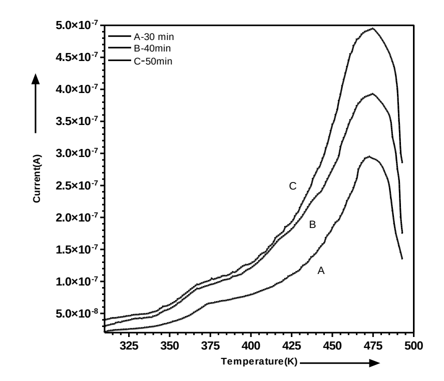


Fig 2.Thermally stimulated current (TSC) spectra of Polyacrylamide

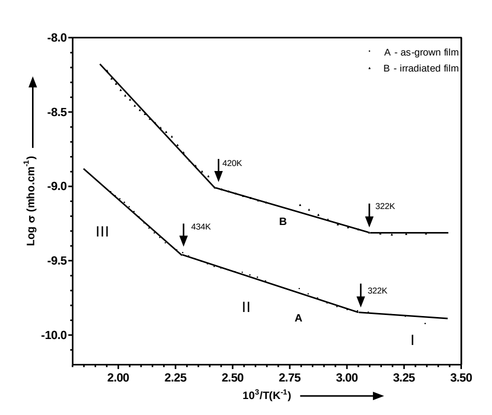


Fig 3.Electrical conductivity in Polyacrylamide

Some of the charged species may be trapped even during the process of polymerization of PAA and are considered to contribute to the electrical conductivity in as-grown PAA films. However, on irradiation, the concentration of the trapped carriers is enhanced and contributes to higher electrical conductivity in irradiated films, as depicted in figure 3. In both the above cases, three distinct regions I, II and III in the conductivity plots have been observed; with the same transition temperatures. Thus the nature of traps and their energy levels being the same; the number of charge carriers trapped is enhanced on irradiation. Further,



International Journal of Engineering Research (ISSN : 2319-6890)
Volume No.2, Issue No.2, pp : 88-90 01 April 2013

the rate of detrapping of charge carriers, on thermal stimulation, for all the three regions in both as-grown and irradiated films is found to be the same; as the plots have the same slopes.

Thermal cleaning of the TSL and TSC curves enabled the analysis of glow curves by the initial rise [8-9] and chen's methods [9-11]; Table 1 shows the activation energies evaluated for the TSL and TSC glow curves.

The activation energies for electrical conductivity, for the three different regions are as given in the Table 2. It can be inferred that the trap energy levels are same for both the as-grown and UV-irradiated PAA.

The differential scanning calorimetry (DSC) in PAA is as depicted in figure 4. Two endothermic peaks have been recorded, the lower temperature peak is considered to be associated with β-relaxation and the higher temperature endothermic peak may be correlated with the α-relaxation in PAA; which are responsible for the observed TSL/TSC glow curves.

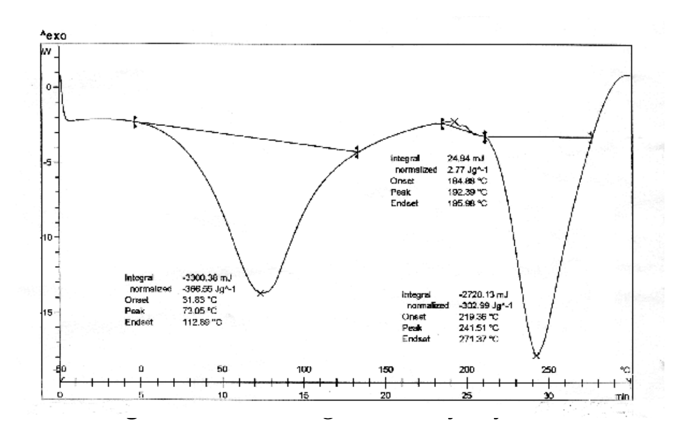


Table 1 . Activation energies for TSL and TSC glow curves

Glow curve Max Temp (K)	TSL		TSC	
	Initial rise method (eV)	Chen's method (eV)	Initial rise method (eV)	Chen's method (eV)
375	0.42	Eω=0.44 Eτ=0.42 Eδ=0.45	0.48	Eω=0.49 Eτ=0.47 Eδ=0.48
475	1.22	Eω=1.23 Eτ=1.24 Eδ=1.26	1.25	Eω=1.25 Eτ=1.26 Eδ=1.23

Table 2 . Activation energies for electrical conduction

Region	Activation energy(eV) (as-grown PAA film)	Activation energy(eV) (UV-irradiated PAA film)
I	0.28	0.3
II	0.9	0.89
III	1.24	1.27

IV. CONCLUSIONS

The primary and secondary relaxations involving large scale and side chain molecular motion respectively; which arise on thermal stimulation of UV-irradiated PAA; facilitate the detrapping of charge carriers; which on recombination with luminescence centers give rise to TSL. These charged species also contribute to TSC curves. Relaxations associated with TSL/TSC are correlated with the two endothermic peaks, recorded by DSC. Thermally stimulated relaxation phenomena in PAA are correlated with electrical conductivity and DSC; to elucidate the mechanism of charge transport in relation to the molecular relaxations in PAA.

REFERENCES

[1]. Charlesby A and Partridge R H , Proc.Roy.Soc **283** 329, 1965
[2]. Tomita A , J. Phys. Soc. Jap **28** 73, 1970
[3]. Hashimoto T, shimada H and Sakai T, Nature, London, **268** 225**,** 1977
[4]. Hashimoto T, Sakai T and Iguchi M , J. Phys. D Appl. Phys **12** 1567, 1979
[5]. Blake A E, Charlesby A and Randle K J , J Phys. D Appl. Phy **7** 759, 1974
[6].Vanderschueren J, Linkens A and Niezette J, J. Polym.Sci pt B , Polym. Phys.**25** 1537, 1987
[7]. Runyan W R , Semiconductor measurements and instrumentation (McGraw Hill) 1975
[8]. Garlick G F J and Gibson A F , Proc. Phy. Soc **60** 574**,** 1948
[9]. Rajendra Prasad K, Int. J. Sci. Engg. & Tech. **1** 301, 2012
[10]. Chen R , J. Appl. Phys **40** 570**,** 1969
[11]. Chen R and Kirsh Y, Analysis of Thermally stimulated processes, Oxford, Peragmon, 1981